# Growth and Photoconductive Characteristics of $CdS_{1-x}Se_x$ Thin Films by the Hot Wall Epitaxy

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## Abstract

The $CdS_{1-x}Se_x$ thin films were grown on the GaAs(100) wafers by a Hot Wall Epitaxy method (HWE). The temperatures the source and the substrate temperature are 580℃ and 440℃ respectively. The crystalline structure of thin films was investigated by double crystal X-ray diffraction(DCXD). Hall effect on the sample was measured by the van der Pauw method and studied on the carrier density and mobility dependence on temperature. In order to explore the applicability as a photoconductive cell, we measured the sensitivity(γ), the ratio of photocurrent to darkcurrent(pc/dc), maximum allowable power dissipation(MAPD), spectral response and response time.

## 1. INTRODUCTION

It is well known that the photosensors are classified into photovoltaic, photoemissive and photoconductive types. The photoconductive type itself consists of bulk effect type and junction type. The CdS and CdSe photoconductive cells[1-2] used in the present work belong to the bulk and the junction types can again be divided by the manufacturing process into the type of sintering, evaporating, depositing, and single crystal. The growth of $CdS_xSe_{1-x}$ thin films on GaAs substrates has been investigated by molecular beam epitaxy (MBE) [3-4], metalorganic chemical vapour deposition (MOCVD) [5-6], and hot-wall epitaxy (HWE) [7-8]. Among these techniques, the HWE has become the most promising technique for the vapour growth of II-VI compounds due to its unique advantage of the thermodynamic equilibrium growth [9-10]. But there have been no reports on the growth of $CdS_xSe_{1-x}$ thin films by Hot Wall Epitaxy method and their photoconductive characteristics.

In this paper, to study characteristics of $CdS_xSe_{1-x}$ thin films, thin films were grown by Hot Wall Epitaxy (HWE). The crystalline structure of thin films were investigated by double crystal X-ray diffraction (DCRD).

Hall effect on this sample was measured by the method of van der Pauw and studied on carrier density and mobility depending on the temperature.

In order to explore the applicability as a photoconductive cell, $CdS_xSe_{1-x}$ thin films were annealed in a Cd-, S-, Se-, Cu-vapour, vacuum, and air atmosphere. We have been measured the sensitivity (γ), the ratio of photocurrent to dark current (pc/dc), maximum allowable power dissipation (MAPD), spectral response and response time.

## 2. EXPERIMENTAL

A home-made hot wall epitaxy apparatus was used for growing the $CdS_{1-x}Se_x$ thin films on the GaAs(100) substrate as shown in Fig. 1. The electric furnace consists of a quartz tube (35mm in diameter) wired with 0.9mm canthal wire. The top part of the tube is used as substrate holder and the bottom part of the tube as source holder. Each part of the tube is connected to the temperature controller (HY AT-96), so as to control the tube temperature independently. Prior to growth on GaAs(100) substrate was cleaned ultrasonically for 1 min in successive baths of trichlororothylene, accetone, methanol and 2-propanol and etched for 1 min in a solution of $H_2SO_4$:$H_2O_2$:$H_2O$(5:1:1). The substrate was degreased in organic solvents and rinsed with deionized water (18.2MΩ). After the substrate was dried off, the substrate was immediately loaded onto the substrate holder in the HWE oven. $CdS_{1-x}Se_x$ thin films were grown by HWE using CdS(Se) (5N. Aldrich) powder. During the growth of $CdS_{1-x}Se_x$ the substrate temperature was maintained at 580℃. and the source temperature was 440℃. The growth rate of the thin films was about 2㎛/h. The grown thin films were analyzed by double crystal X-ray diffraction (Bede Scientific co. FR590) to obtain the optimum growth condition. The thickness of the grown $CdS_{1-x}Se_x$ thin films was measured by a α-step profilometer (Tencor , α-step 200).

Hall effects measurements were performed using the van der Pauw method.

To study characteristics of $CdS_{1-x}Se_x$ photoconductive cells, $CdS_{1-x}Se_x$ thin film were annealed in a Cd-, S-, Se-, Cu-vapour, vacuum, and air atmosphere. The annealing conditions are given in table 1.

Table 1. Annealing conditions

| Samples | Annealing condition |
|---|---|
| CdS | (unannealed) |
| CdS : Cd | Cd 0.0015g, 300℃, 3hr ($10^2$torr < Cd vapour < $10^3$torr) |
| CdS : S | S 0.0015g, 900℃, 3hr ($10^3$torr < S vapour < $10^4$torr) |
| CdS : Cu | Cu 0.0015g, 900℃, 3hr (Cu vapour pressure ~ $10^{-8}$torr) |
| CdS : vacuum | vacuum, 900℃, 3hr |
| CdS : air | air, 600℃, 3hr |
| CdSe | (unannealed) |
| CdSe : Cd | Cd 0.0015g, 400℃, 30min (Cd vapour pressure ~ $10^{-6}$torr) |
| CdSe : Se | Se 0.0015g, 750℃, 30min (Se vapour pressure ~ $10^1$torr) |
| CdSe : Cu | Cu 0.0015g, 900℃, 3hr |
| CdSe : vacuum | vacuum, 600℃, 1hr |
| CdSe : air | air, 300℃, 30min |

In order to measure the photoconductive characteristics of the $CdS_{1-x}Se_x$ thin films grown on the GaAs(100) substrate, this sample was measured at room temperature. The halogen lamp (650W) has been used as a light source. This source can be filtered by the light chopper (PAR.192) and the monochromator (Jarrel Ash, 82-020). When the mono-spectrum is incidented on the sample, the spectrum has been measured by the X-Y recorder (Rigaku-denki, RE-201T) after amplifying the current with the lock-in amplifier (E G & G, 5210).

## 3. RESULTS AND DISCUSSION

3-1. Growth parameters and structure characteristic of $CdS_{1-x}Se_x$ thin films.

After the substrate was chemically etched, to make an optimum surface state prior to growth, the substrate was annealed from 520℃ to 600℃ with 2 0℃ steps and the annealing time was varied from 10 to 30min to remove the residual oxide on the surface of substrate. After heat treatment, the surface of the substrate was annealed at 580℃ for 20min. After the optimum surface heat treatment, to find the best growth condition, thin films were grown while the source tempreature was kept at 630℃, 650℃, and 68 0℃, respectively, and the substrate tempreature was changed from 380℃ to 440℃. After preparing $CdS_{1-x}Se_x$ thin films on GaAs(100) substrate, we investigated the crystal quality of the grown thin films as a function of the growth condition.

From the results of the X-ray double crystal rocking curves (DCRC), the best growth condition is determined when the full width at half maximum (FWHM) of the grown thin films shows a minimum. We obtained a minimum FWHM value of 267 arcsec for the optimum grown thin films with a thickness of 4㎛ in the X-ray rocking curves, as shown Fig. 2. The electrical transport properties were determined by Hall effect measurement in the van der Pauw geometry. The Hall measurement results show that the carrier density of CdS, $CdS_{0.47}Se_{0.53}$, CdSe were $6.48\times10^{23}/m^3$, $9.61\times10^{22}/m^3$, $1.89\times10^{23}/m^3$, and the mobility of CdS, $CdS_{0.47}Se_{0.53}$, CdSe were $1.61\times10^{-2}$ $m^2/vs$, $2.66\times10^{-2}$ $m^2/vs$, $1.92\times10^{-2}$ $m^2/vs$ at room temperature resppectively, as shown in table 2~4.

From Hall data, in case of CdS, the mobility was decreased in the temperature range 30K to 200K by piezoelectric scattering and decreased in the temperature range 200K to 293K by the polar optical scattering [11], as shown in Fig. 3.

In case of $CdS_{0.47}Se_{0.53}$ the mobility was increased in the temperature range 30K to 130K by impurity scattering and decreased in the temperature range 130K to 293K by the lattice scattering, as shown in Fig. 4.

In case of CdSe, the mobility was increased in the temperature range 30K to 150K by impurity scattering and decreased in the temperature range 200K to 293K by the lattice scattering, as shown in Fig. 5.

Activation energy($E_d$) obtained from ln n of carrier density versus 1/T for CdS, $CdS_{0.47}Se_{0.53}$, and CdSe, as shown in Fig. 6~8. The value of activation energy are 0.51eV, 0.28eV and 0.19eV, respectively.

We measured the value of component rate growing by mole ratio of $CdS_{1-x}Se_x$(CdS, $CdS_{0.50}Se_{0.50}$, CdSe) thin film as EDS(energy dispersive X-ray microanalysis) (Link, AN-10-85S). They have been shown to grown as CdS, $CdS_{0.47}Se_{0.53}$, CdSe.

3-2. Spectrum response

We measured spectrum response of $CdS_{1-x}Se_x$ photoconductive cell at room temperature, as shown in Fig. 9. $CdS_{1-x}Se_x$ photoconductive cell is distributed over slope of curve on the range of long wavelength and also it has a sensitivity at near infrared region as the quantity of Se increases. The peak position of spectrum in Fig. 9 is shown in table 5. When the temperature of CdS thin film is 293K, we analyzed peak position of 506nm(2.4500eV). The position of 505nm(2.4551eV) is peak position by excited electron from valance band $\Gamma_9$(A) to conduction band $\Gamma_7$ at 293K. As exciton-binding energy[12] is 0.029eV, when n=1, free exciton spectrum may be positioned at 2.4261eV(2.4551-0.029) and free exciton spectrum $A_2$ spectrum may be positioned at 2.4479eV($2.4551-0.029/2^2$). Exciton $A_2$ spectrum, 2.4479eV was approximatly coincided with the peak 506nm(2.4500eV) spectrum within the error range 0.0051eV, so we knew photocurrent 506nm spectrum was free exciton $A_2$ spectrum. We measured peaks conformed to those of $CdS_{0.47}Se_{0.53}$ as photocurrent peaks by electron excited from valance band $\Gamma_9$(A) to conduction band $\Gamma_7$, and also measured peaks conformed to those of CdSe as photocurrent peaks by electron excited from valance band $\Gamma_7$(B) to conduction band $\Gamma_7$.

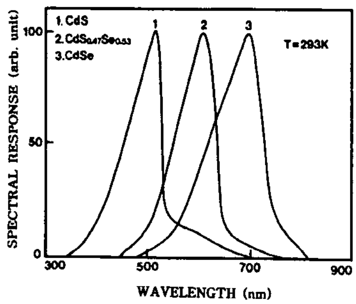


Fig. 9. Photocurrent spectra of $CdS_{1-x}Se_x$ thin film (1) CdS, (2) $CdS_{0.47}Se_{0.53}$, (3) CdSe

**Table. 5** Photocurrent peak energy and fine structure of $CdS_{1-x}Se_x$ thin film

| $CdS_{1-x}Se_x$ | pc peak position (nm) | (eV) | fine structure of photocurrent |
|---|---|---|---|
| CdS | 506 | 2.450 | free excition $A_2$ |
| $CdS_{0.47}Se_{0.53}$ | 608 | 2.039 | $\Gamma_9(A) \rightarrow \Gamma_7$ |
| CdSe | 709 | 1.749 | $\Gamma_7(B) \rightarrow \Gamma_7$ |

3.3. The characteristic of $CdS_{1-x}Se_x$ photoconductive cell

3.3.1 sensitivity

Sensitivity of photoconductive cell is a relation between intensity of incident illumination to photoconductive surface and out put from the cell. Sensitivity can be expressed by current and resistance of the cell, and it is common to denote sensitivity as resistance of cell. We used tungsten lamp as light source, and then measured the resistance of cell by adjusting illumination gradually from 10lx to 1000lx.

We named ɤ characteristic as linear gradient at the relation of intensity of illumination and resistance, and it is

$$\gamma_{10}^{1000} = \tan\Theta = \frac{\log R_{10} - \log R_{1000}}{\log 1000 - \log 10}$$

Where, $R_{10}$ and $R_{1000}$ are resistance of one each, when intensity of illumination is used with 10lx and 1000lx. We illuminated the relation between the resistances of cells measured by changing the lighted intensity of illumination from 10lx to 1000lx. They, (a) vacuum, (b) Cu, (c) S, (d) Cd, and (e) air in Fig. 10, are shown cells resistances according to illumination of the annealed CdS cell. At this time, the values of ɤ are (a) 0.38, (b) 0.98, (c) 0.84, (d) 0.74, and (e)0.90, respectively.

They, (a) Cd, (b) S, (c) Se, (d) Cu, (e) vacuum, and (f) air in Fig. 11, are shown cells resistance according to illumination of the annealed $CdS_{0.47}Se_{0.53}$ cell. At this time, the values of ɤ are (a) 0.87, (b) 0.84, (c) 0.86, (d) 0.99, (e) 0.25, and (f) 0.93.

They, (a) vacuum, (b) Cu, (c) Se (d) air, and (e) Cd in Fig. 12, are shown cells resistance according to illumination of the annealed CdSe sample. At this time, the values of ɤ are (a) 0.27, (b) 0.97, (c) 0.86, (d) 0.92, and (e) 0.78, respetively.

In the sample annealed under Cu vapour the sensitivity of the characteristics was best.

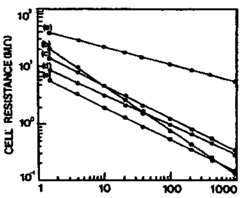


Fig. 10. Cell resistance vs illumination characteristics of CdS (a) Vacuum, (b) Cu, (c) S, (d) Cd, and (e) air

3.3.2 Maximum Allowable Power Dissipation (MAPD)

This is maintained linear with illumination current as long as we irradiated constant intensity of light on photoconductive cell and changed D.C. input voltage.

When the in-put voltage is increased gradually from 1V, it is lineared, then it is deviated. We defined its phenomenon as MAPD and denote its unit mW. We illuminated the relation between in-put voltage and current by irradiation of light of annealed CdS thin films in Cu vapour, as shown in Fig. 13. When we fixed intensity of illumination at 300lx, 500lx, and 800lx and increase gradually in-put voltage from 1V, it is kept linear within 100V, 71V and 53V at 300lx, 500lx, and 800lx, and then MAPD measured 318mW. The annealed sample in S-, Cd-vapour, vacuum, and air atmosphere were measured by this method. MAPD of annealed samples are 118mW, 106mW, 18mW, and 245mW respectively, and the annealed samples in Cu vapor have the biggest value of MAPD. We illuminated the relation between in-put voltage and the current by irradiation of light of the annealed $CdS_{0.47}Se_{0.53}$ thin films in Cu vapour, as shown in Fig. 14. When we fixed the intensity of illumination at 300lx, 500lx, and 800lx and increase gradually in-put voltage from 1V, it is kept linear within 100V, 75V and 51V at 300lx, 500lx, and 800lx, and then MAPD was measured as 342mW. When the annealed samples in Cd-, S-, Se-vapour, air, and vacuum atmosphere were measured from this method, MAPD of annealed samples was obtained 121mW, 118mW, 108mW, 264mW, and 18mW respectively, and the annealed samples in Cu vapor have the biggest value of MAPD. .

We illuminated the relation between in-put voltage and the current by the irradiation of light of annealed CdSe thin films in Cu vapour, as in shown Fig. 15. When we fixed the intensity of illumination at 300lx, 500lx, and 800lx and increase gradually in-put voltage from 1V, it was kept linear within 100V, 78V and 55V at 300lx, 500lx, and 800lx respectively, and then MAPD measured 335mW. The annealed samples in Cd-, Se-vapour, vacuum, and air atmosphere measured from this method, MAPD of annealed sample is 108mW, 198mW, 21mW, and 251mW respectively, and the annealed samples in Cu vapor have the biggest value of MAPD.

When MAPD is big, it means appling fields are extensive, though the in-put voltage is increased in connecting circuit and it is because of the maintained range as linear

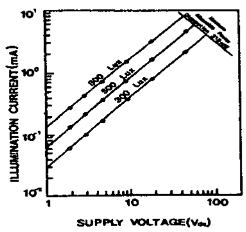


Fig. 13. Illumination current vs voltage characteristics of CdS thin films annealed in Cu vapour.

3.3.3 pc/dc

We measured the ratios of the dark current (dc) of the in-put voltage (1.5V), to the photocurrent (pc) the illuminated white light (3000lx) on an annealed samples in Cd-, S-, Se-, Cu-vapour, vacuum and air atmosphere, as shown in table 6~8.

Since, the biggest ratio value of the photocurrent versus the darkcurrent is that of the annealed CdS cell in Cu vapour, it is expected as a good photoconductor, for its value of the ratio (pc/dc) is $9.42 \times 10^6$.

Since, the biggest ratio value of the photocurrent versus the darkcurrent is that of the annealed $CdS_{0.47}Se_{0.53}$ *cell in* Cu *vapour, it is expected* as a good photoconductor, for its value of the ratio (pc/dc) is $1.67 \times 10^7$.

Since, the biggest ratio value of the photocurrent versus the darkcurrent is that of the annealed CdSe cell in Cu vapour, it is expected as a good photoconductor, for its value of the ratio (pc/dc) is$1.37 \times 10^7$. The minimum value as practical use is $10^5$[13].

**Table 6**. Comparison of darkcurrent with photocurrent of CdS thin film grown by HWE method annealed in Cd, S, Cu atmosphere and vacuum (light intensity : 3,000 lx)

| sample | darkcurrent (A) | photocurrent (A) | ratio (pc/dc) |
|---|---|---|---|
| CdS | $1.87\times10^{-3}$ | $2.30\times10^{-3}$ | $1.23\times10^{0}$ |
| CdS : Air | $8.34\times10^{-6}$ | $6.40\times10^{-1}$ | $7.67\times10^{4}$ |
| CdS : Vacuum | $6.35\times10^{-3}$ | $2.22\times10^{-1}$ | $3.50\times10^{1}$ |
| CdS : Cd | $7.28\times10^{-5}$ | $3.37\times10^{-2}$ | $4.63\times10^{2}$ |
| CdS : S | $6.37\times10^{-6}$ | $1.35\times10^{-1}$ | $2.12\times10^{4}$ |
| CdS : Cu | $1.73\times10^{-7}$ | $1.63\times10^{0}$ | $9.42\times10^{6}$ |

3.3.4 Response Time

The response time can defined into two things, 'rise time' required for the value of the current to reach the 63% of the peak with being illuminated light to the photoconductive cell and 'decay time' required till the peak value *become 37% after being removed* light. This 'decay time' is called carrier life when light (10 lx) illuminated on $CdS_{1-x}Se_x$ photoconductive cell made by HWE. In case of CdS, the response time was the best for the sample annealed in Cu vapour, compared with in Cd-, S-, Cu-vapour, air, and vacuum atmosphere. Then we obtained the rise and decay time of 10ms and 9ms as shown in table 9. In case of $CdS_{0.47}Se_{0.53}$, the response time was the best for the sample annealed in Cu vapour, compared with the sample annealed in Cd-, S-, Se-, Cu-vapour, air, and vacuum atmosphere. Then we obtained the rise and decay time of 9.5ms and 9.1ms, as shown in table 10.

In case of CdSe, the response time was the best for the sample annealed in Cu vapour, compared with in Cd-, Se-, Cu-vapour, air, and vacuum atmosphere. Then we obtained the rise and decay *time of* 10ms and 9.5ms, as shown in table 11.

Response time can be practical to be used within 20ms of rise time, and the decay time[13]. Response time depends on intensity of light, load resistances, conditions of crystal deposition, temperatures, and so on.

**Table 9**. Response time of CdS thin film

| sample | 10 lx | |
|---|---|---|
| | rise time (ms) | decay time (ms) |
| CdS : Cd | 22 | 20.6 |
| CdS : S | 16 | 12 |
| CdS : Cu | 10 | 9 |
| CdS : air | 13 | 10 |
| CdS : vacuum | 33 | 29.3 |

## 4. CONCLUSION

We had grown $CdS_{1-x}Se_x$ thin film by HWE method, and it was annealed in Cd, S, Se, Cu- vapour, air, and vacuum atmosphere. After that, we studid the characteristic of physical characteristic and photoconductive cell.

The results were following

1) When the temperature of the substrate was 420℃, and the temperature of the evaporation source was 580℃, full width at half maximum value was 267arcsec, and it was the best growth condition because it was the smallest value.

2) In case of CdS, $CdS_{0.47}Se_{0.53}$, and CdSe, activation energy obtained from ln n versus 1/T of carrier density were 0.51eV, 0.28eV, and 0.19eV, respectively. From Hall data, in case of CdS, the mobility was decreased in the temperature range 30K to 200K by *piezoelectric scattering* and decreased in the temperature range 200K to 293K by the polar optical scattering. In case of $CdS_{0.47}Se_{0.53}$ the mobility was increased in the temperature range 30K to 130K by impurity scattering and decreased in the temperature range 130K to 293K by the lattice scattering. In case of CdSe, the mobility was increased in the temperature range 30K to 150K by impurity scattering and decreased in the temperature range 200K to 293K by the lattice scattering.

3) The results indicated that the photoconductive characteristic were the best for the sample in Cu vapour compare with Cd-, S-, Se-vapour, vacuum, and air atmosphere of $CdS_{0.47}Se_{0.53}$ thin films. We obtained the sensitivity of 0.99, the value of pc/dc of $1.67\times10^7$, the MAPD of 342mW, and the rise time and decay time of 9.5ms *and* 9.1ms, *respectively*.

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